Coping with T30 Obsolescence in 2013

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Coping with T30 Obsolescence in 2013

- Background
- Coping since 2007
- Options for Coping after 2013
  1. *Extending the shelf life of the emulsion*
     - Tests in Work
  2. *Extending the shelf life of plates*
  3. *Extending the shelf life of unactivated cells*
  4. *Extending the shelf life of activated cells*
     - Testing with ISS Cells
  5. *Building cells with new emulsions*
     - Characterizing Candidate Emulsions
     - Results of Stress Cycling Tests with Cells made with T30 and TE3859
- Concluding Remarks

Background

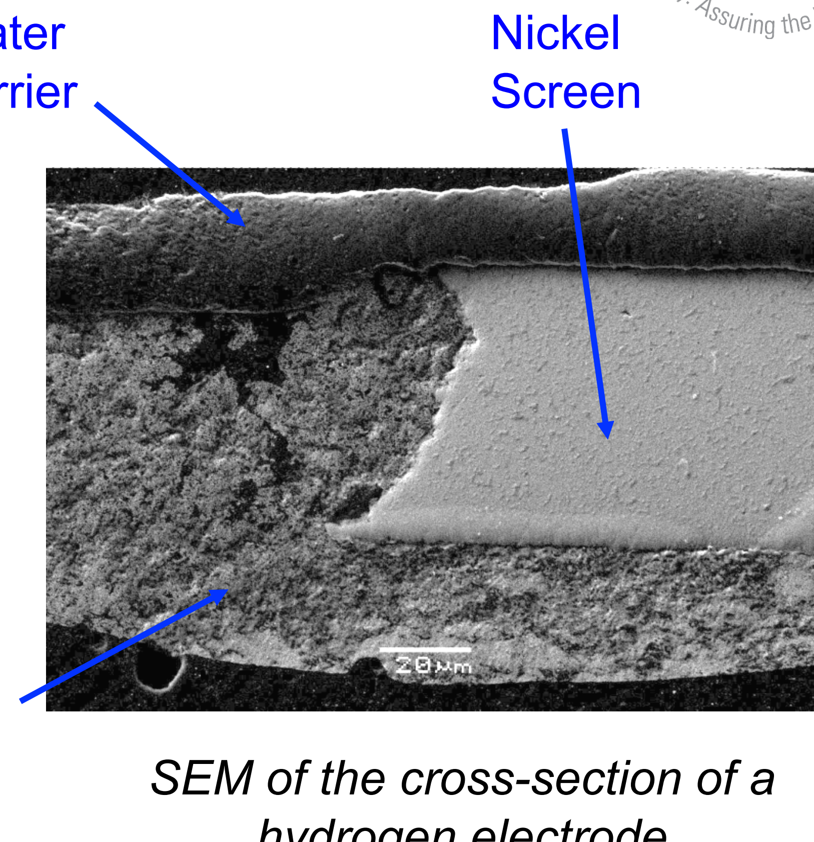
- In 2006, Dupont announced that T30, a Teflon emulsion used to support the active material in hydrogen electrodes would be removed from the commercial market in 2007
  - *T30 PFOA (perfluorooctanoic acid) and Triton X-100 surfactant undesirable due to environmental concerns*

- Test electrodes were made with Dupont's recommended replacement at the time, TE3859, but interest in qualifying this compound dwindled when it became clear that this, too, would be unavailable in 2013 when further restrictions regarding the use of PFOA in the manufacturing process would be applied

- The Teflon component is critical to the performance of the hydrogen electrode because it stabilizes the gas/liquid/solid interface needed to sustain the charge and discharge reactions
  - *Too much surface coverage and the electrode may run dry*
  - *Insufficient surface coverage and the electrode may flood*

Nickel-Hydrogen Cell Hydrogen Electrode

- Hydrogen electrode composition
  - *Nickel screen current collector to provide high conductivity*
  - *Porous polymer membrane on the backside to retard water loss and facilitate hydrogen flow*
  - *Pt/Teflon active material to reversibly catalyze the conversion of water to hydroxide and hydrogen*

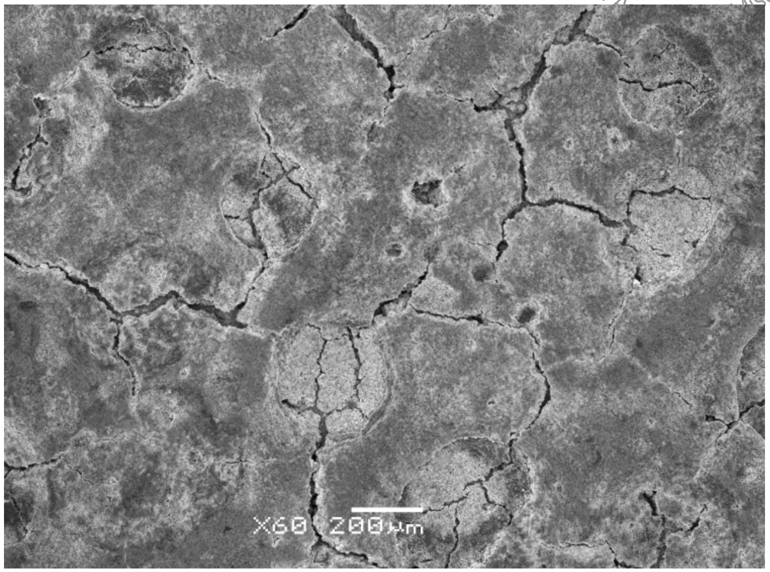


SEM of the cross-section of a hydrogen electrode

Failure Modes Associated with Hydrogen Electrodes

- Alkaline Fuel Cell Applications
  - *Excessive hydrophilic nature – flooding*
  - *Excessive hydrophobic nature – insufficient wetting*
  - *Flooding due to water vapor accumulation*
    - More commonly a concern at higher temperatures
  - *Recrystallization of Pt particles over life*
    - Lowers reactivity and catalyst surface area
  - *Oxidation and dissolution of platinum*
  - *Carbon dioxide poisoning - usually from impure reactant gases*
  - *Silicate build-up from asbestos wicks*

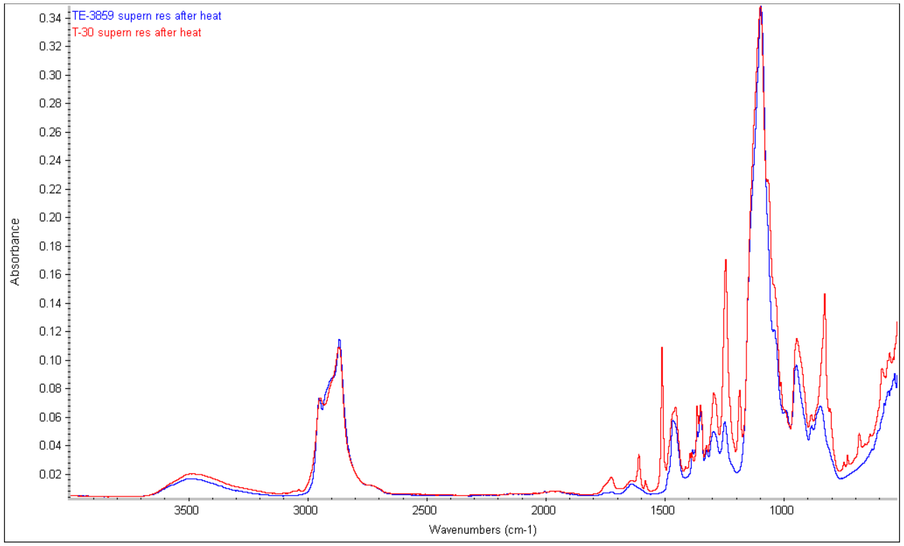
- Battery Applications
  - *Shorting due to Pt particle dislocation*



SEM Image of the top surface of a hydrogen electrode

Comparison of T30 with TE3859 Replacement

- Analysis of Trace Components
  - *FTIR analysis confirmed that T30 contained volatiles consisting of phenol ethoxylates; octyl, nonyl and decyl phenol ethoxylates*
  - *FTIR analysis confirmed that TE3859 contained polyethylene glycol monomethyl ether*
- Different volatility of new surfactants is likely to affect final surface area and pore size distribution for the same sintering temperatures
- Effect of different class of surfactants on electrode life is unknown
  - *Ability to wash residues from electrodes also unknown*



FT-IR spectra of the T-30 and TE-3859 residues of the centrifuged supernatant heated to 120^{o}C

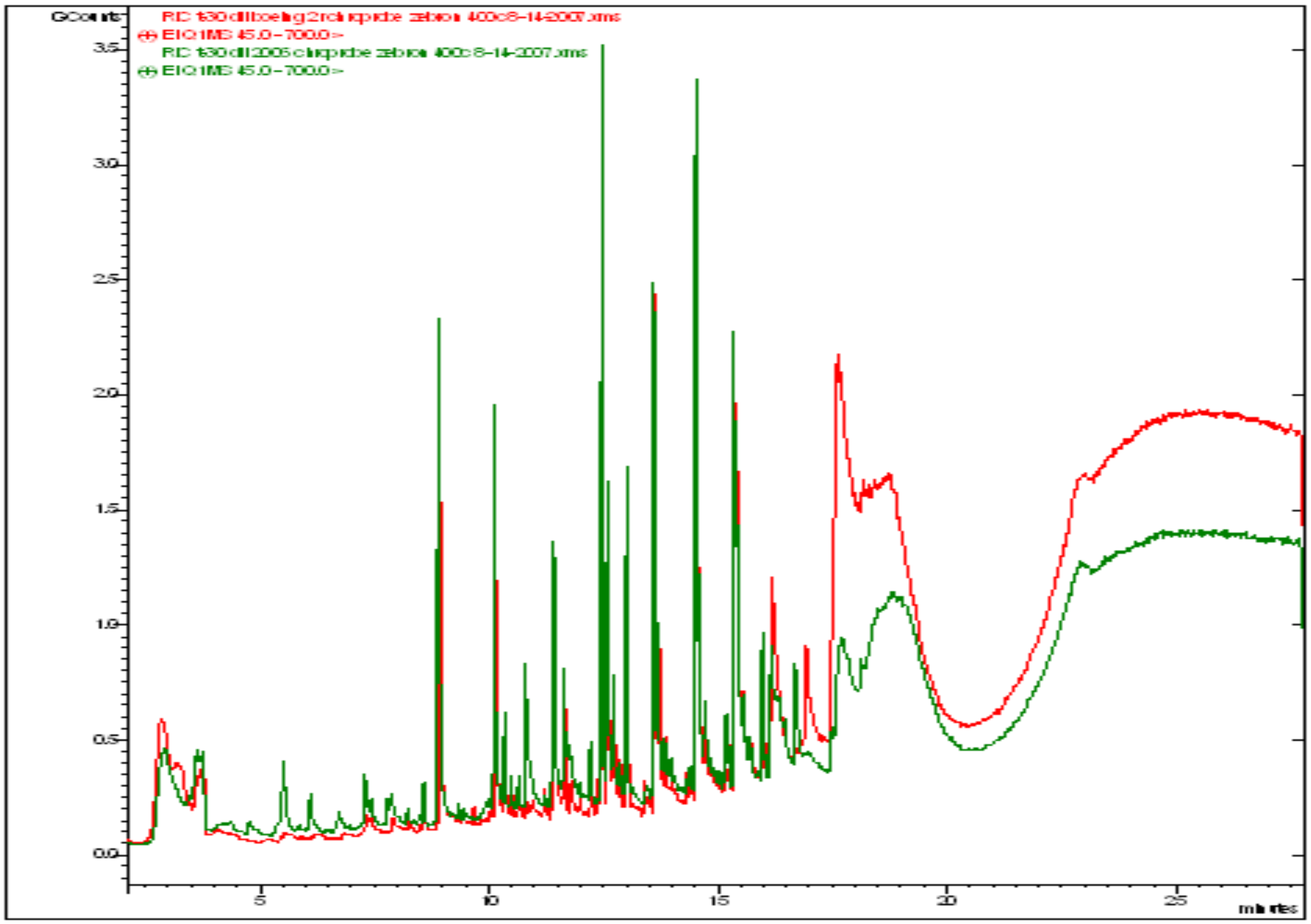
Coping since 2007

- Late 2006, the means of obtaining small amounts of T30 emulsion through 2012 were established
  - *This material has been provided to US nickel-hydrogen battery manufacturers at roughly six month intervals*
  - *The shelf life of each production batch has been limited to 6-12 months even with special storage techniques including refrigeration and periodic mixing*
  - *Aerospace has samples from every batch made to date to verify the composition using FTIR and GC-MS*
    - The chemical changes in the surfactant used in these batches have also been studied as these samples accumulate age

Comparison of fresh (red) and aged (green) T30 surfactant samples

50 YEARS
Honoring the Legacy. Assuring the Mission.

Overlaid Chromatogram Plots



Options for Coping after 2013

1. Extending the shelf life of the emulsion
   - *Key Concerns*
     - pH changes due to break-down of the surfactant and side reactions
     - Coagulation of the monomer
   - *Tests in Work*
     - Five 1-gallon samples from the same manufacturing lot are being stored under different conditions of temperature, inert gas, and pH.
       - *All samples are periodically rolled in their containers*
     - Testing initiated August 2010
     - Testing for bulk density, pH, chemical composition, and monomer coagulation scheduled every six months
       - *First round of tests will be in January*

Options for Coping after 2013

2. Extending the shelf life of plates
   - *This option can be attractive to programs with limited needs*
   - *Concerns for this approach are:*
     - Proper storage techniques (inert gas, weld-sealed containers, etc.)
     - Distortion of plates under static loads (i.e. “Cold Flow”)
     - High up-front costs for materials
     - Longevity of extended storage – how long can the qualification status last?

Options for Coping after 2013

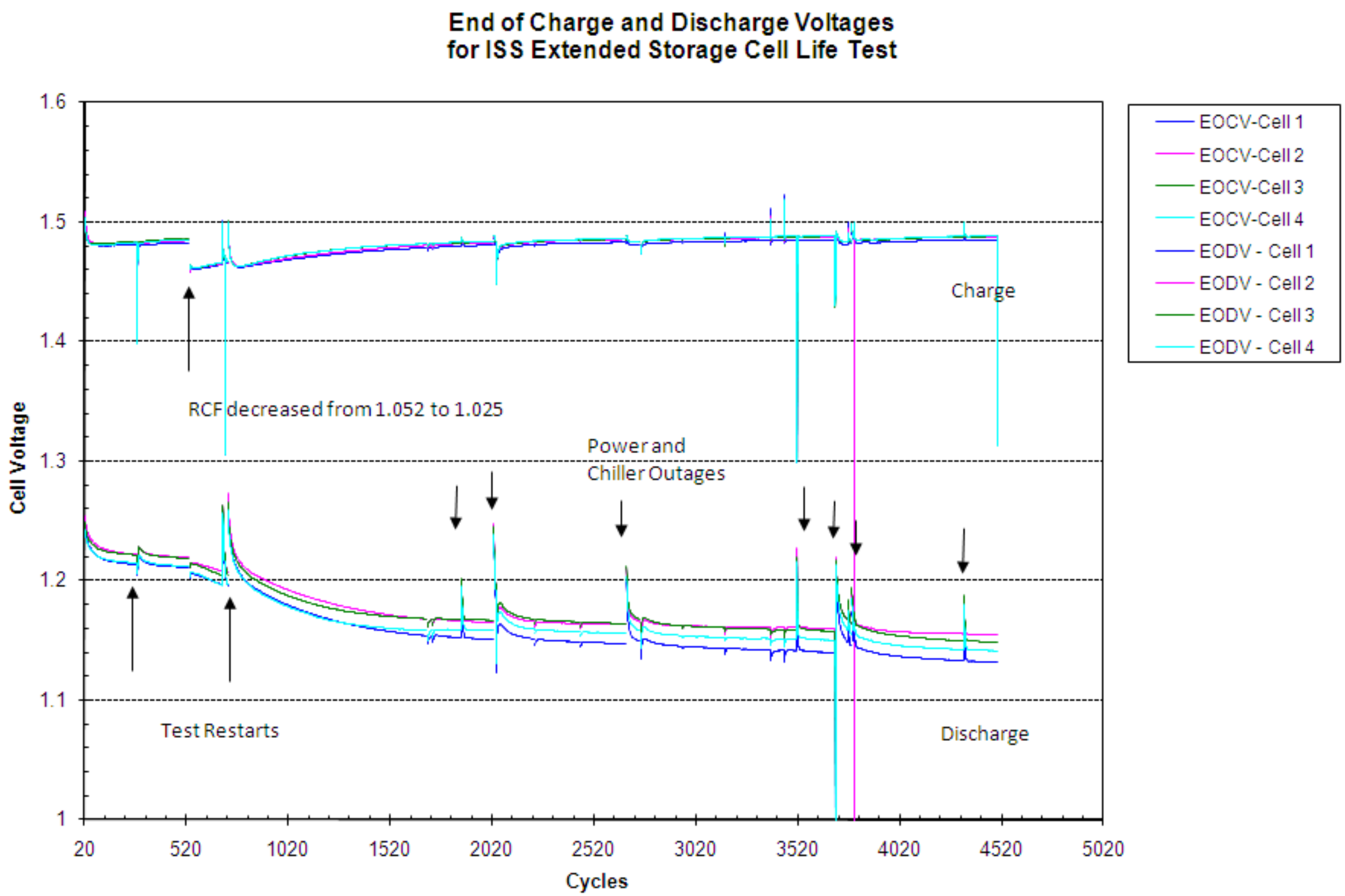
3. Extending the shelf life of unactivated cells
   - *This option can be attractive to programs with limited needs*
   - *Concerns for this approach are:*
     - Proper storage techniques (such as cover gas)
     - High up-front costs for materials
     - Longevity of extended storage – how long can the qualification status last?

Options for Coping after 2013

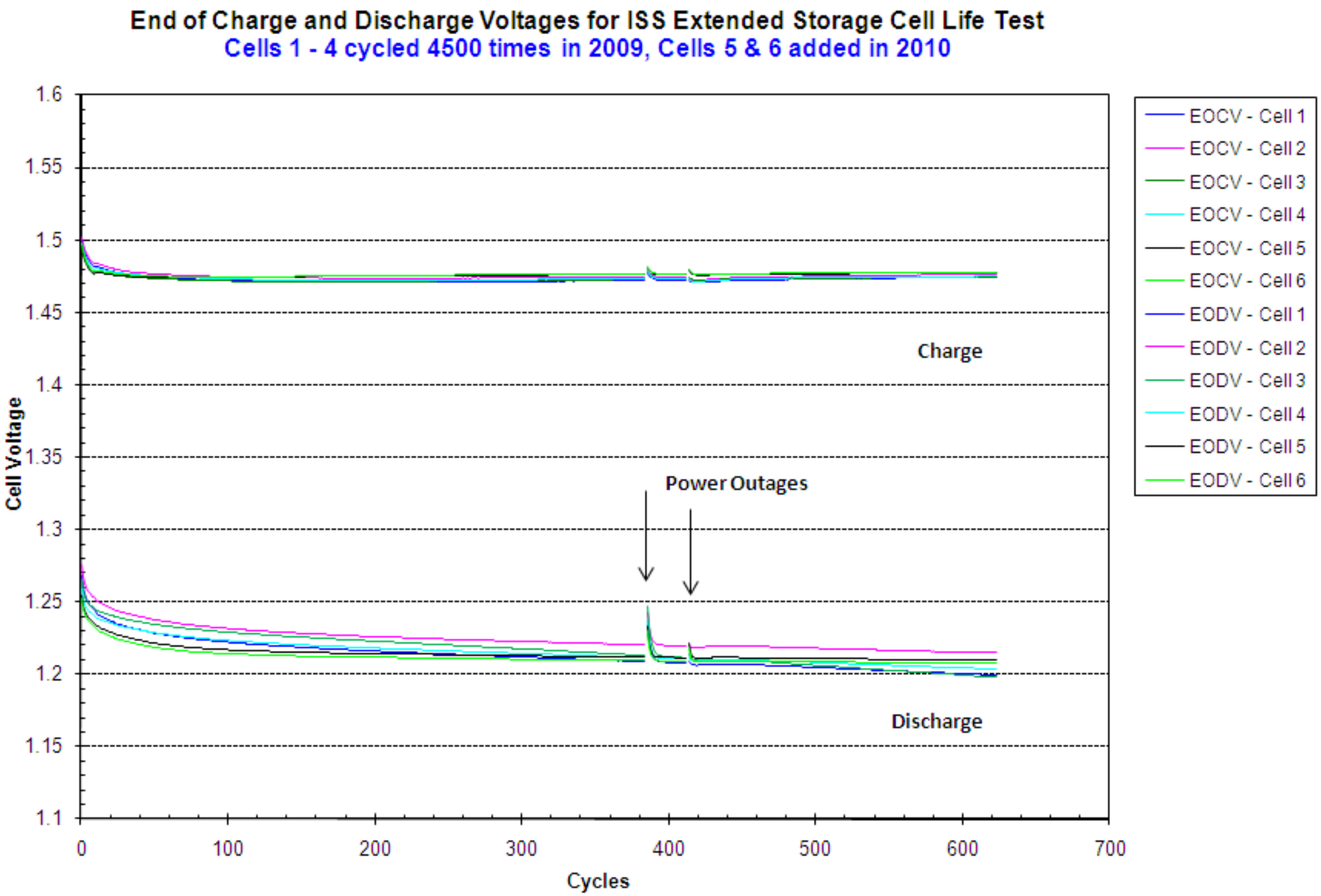
4. Extending the shelf life of activated cells
   - *NASA has successfully tested and flown nickel-hydrogen batteries activated and stored well-ahead of need for some of their programs with sliding launch dates*
   - *In 2008, The Aerospace Corporation was fortunate to receive 16 of the left-over ISS cells from NASA-Glenn*
     - *Twelve 81Ah, cells manufactured by EP*
     - *Cells already have five years cumulated refrigerated storage with only acceptance tests run on them prior to storage*

- Life testing was initiated on four cells in June 2009, and two more cells were added in June 2010
  - *The remaining six cells are in refrigerated storage*
  - *The cycle tests in 2009 used a 35% DOD (42A + 62A discharge, and a 1.025 RCF (34A charge to time limit and taper) at 5^{o}C to simulate other NASA life tests*
  - *In June 2010, the RCF was increased to 1.042 due to walk-down seen in the pressure date*
    - 4500 cycles accumulated to in 2009 on first four cells
    - 630 cycles accumulated since other two cells added

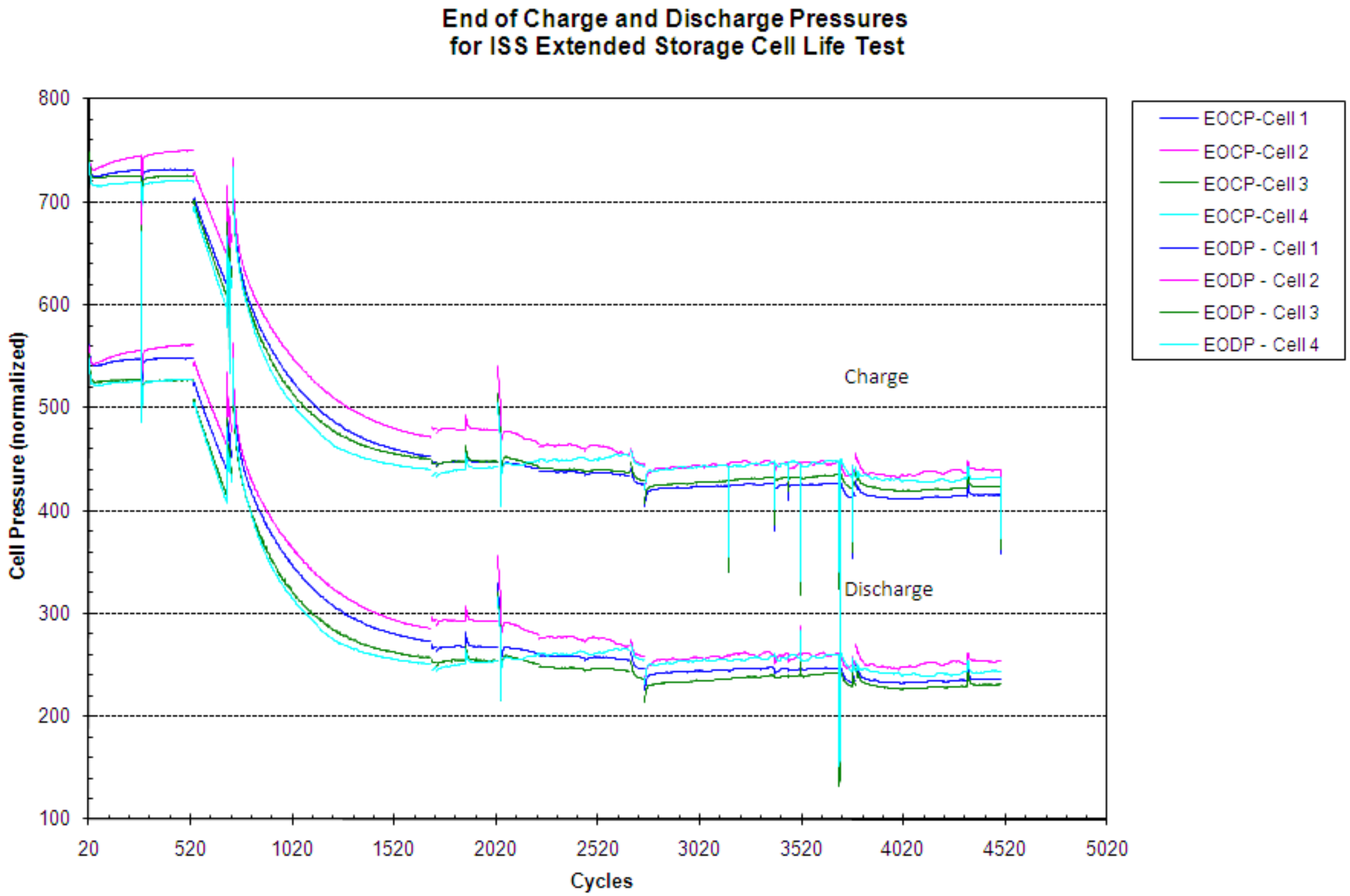
Voltage Trends in 2009 ISS Cell Life Test



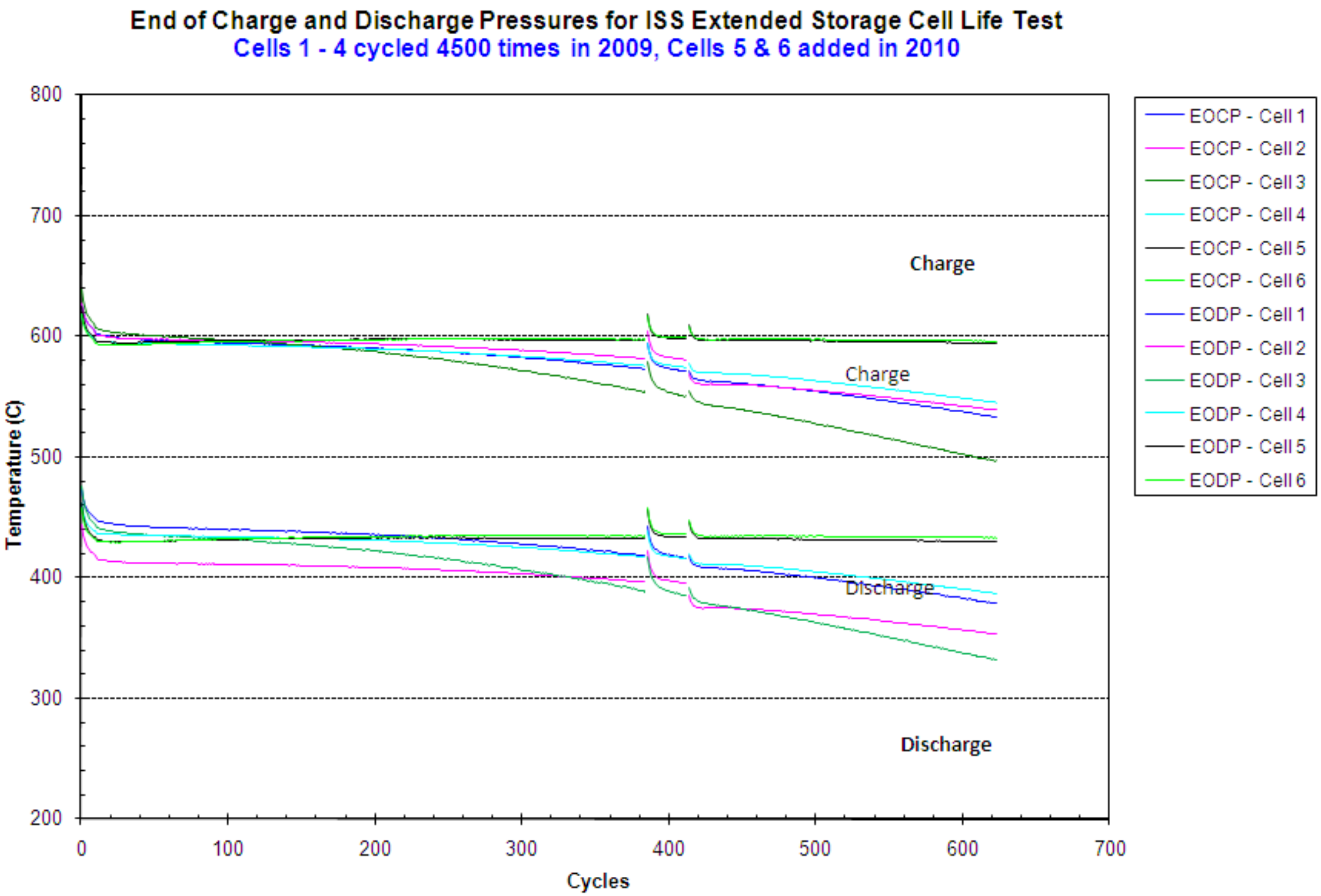
Voltage Trends in 2010 ISS Cell Life Test



Pressure Trends in 2009 ISS Cell Life Test



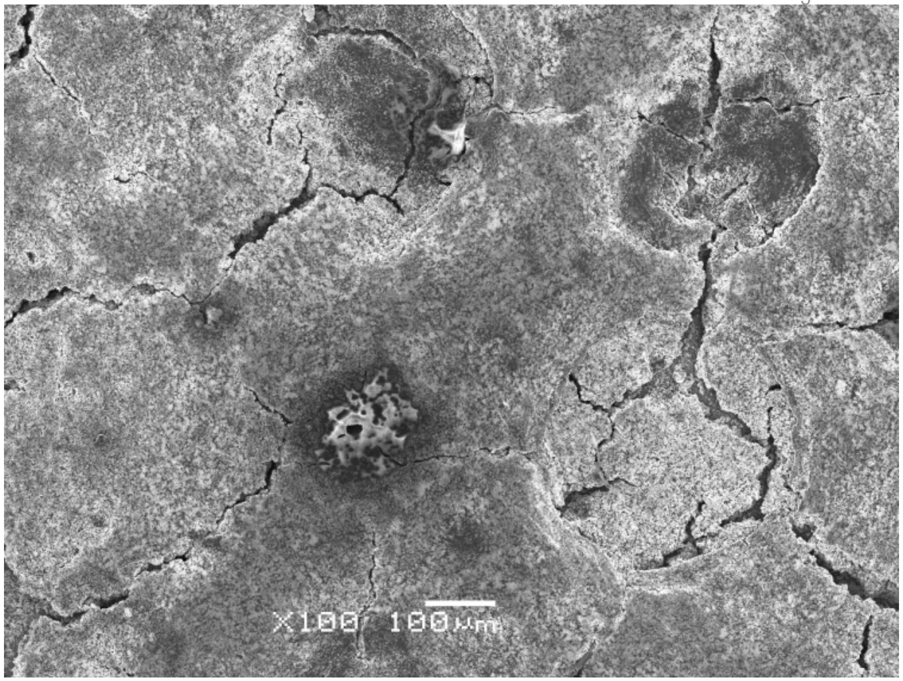
Pressure Trends in 2010 ISS Cell Life Test



Options for Coping after 2013

5. <u>Building cells with new emulsion</u>
  - *Characterizing new emulsions*

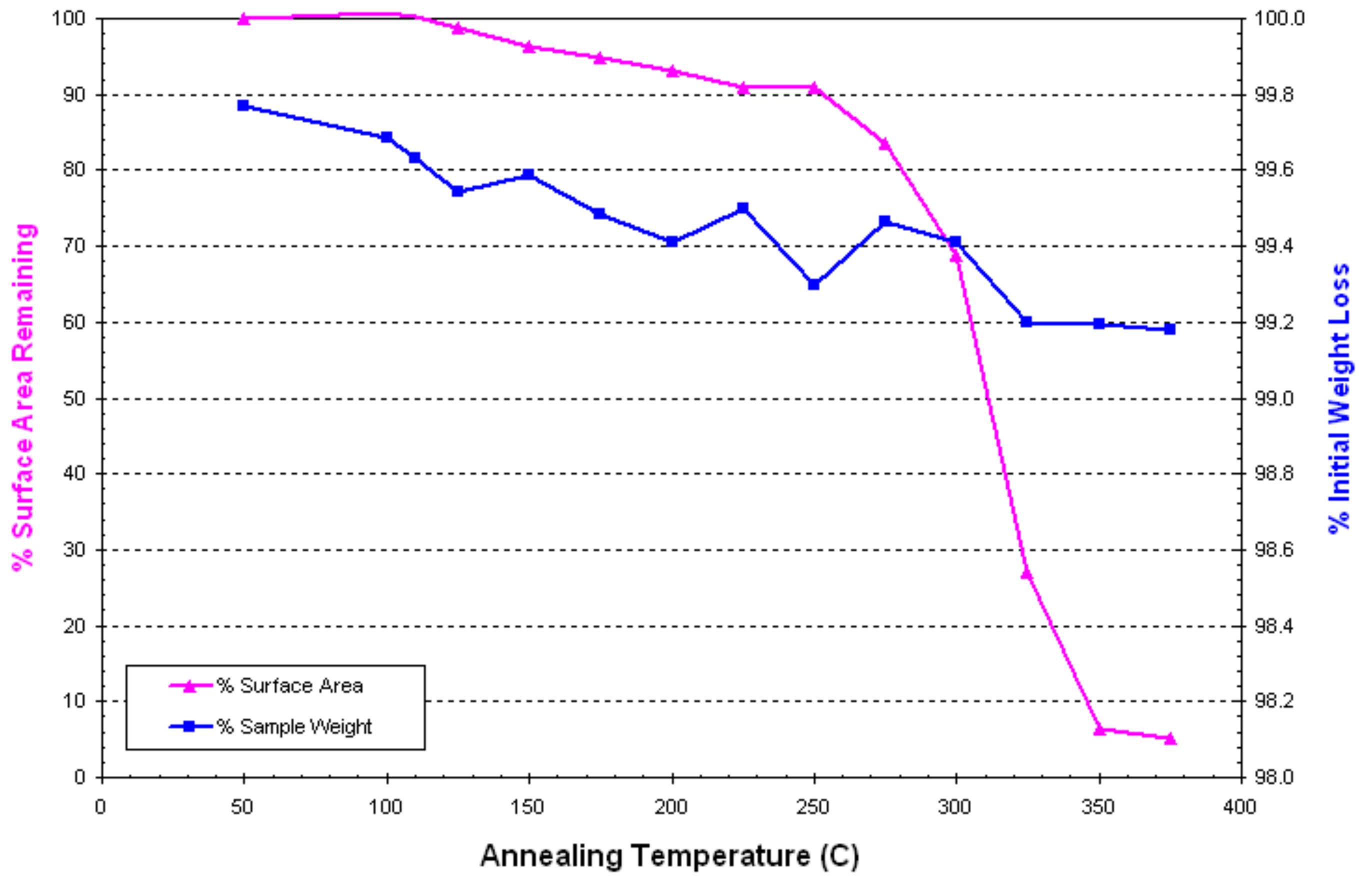
- Emulsions that produce a similar microstructure, pore size distribution, and structural integrity as T30 does on electrodes are likely good candidates for replacing T30
  - *Some of these properties are driven by the surfactant*
  - *Some of these properties are driven by process variables such as sintering temperature, compaction pressures, and slurry composition*



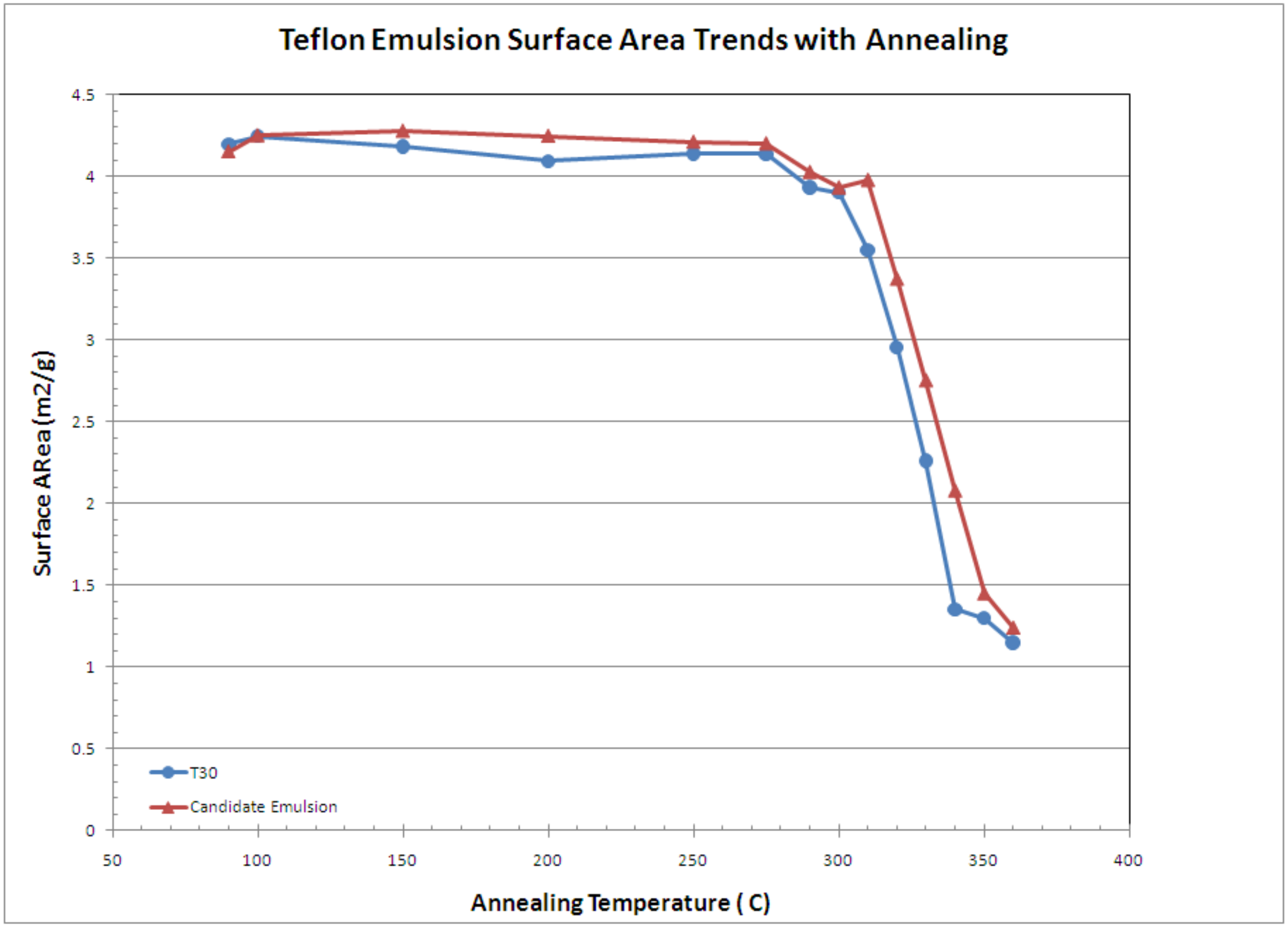
SEM Image of the top surface of a hydrogen electrode with residue left in surface crater

Gas physisorption was used to study the surface are of T30 electrodes as a function of annealing temperature on pre-fabricated Hydrogen Electrodes:

Transition discovered at ~ 250^{o}C



Technique was used to study the difference in transition between one electrode made with T30 and a candidate emulsion last spring: No significant difference found



Characterizing new emulsions (cont.)

- There are still a large number of variables to study when candidate emulsions become available. Principle among these are:
  - *Handling characteristics of the emulsions*
  - *Rate of coagulation with storage*
- Material properties of the fabricated electrodes
  - *Density, pore size distribution, phase distribution of Teflon and Pt, adhesion to substrate, surface appearance*
  - *KOH retention and gas permeability*
  - *Organic impurities*
- Electrical properties
  - *Conductivity*
  - *Oxygen and hydrogen overpotential*

Options for Coping after 2013

5. Building cells with new emulsion

– *Results of stress cycling with cells made with T30 and TE3859 emulsions*

- Four 90Ah cells were received from EP for evaluation
  - *RNH90, double zircar separator, wall wick, 31% KOH, and strain gages*
  - *Two made with T30 (cells 1, 4) and two with TE3859 (cells 2 & 3)*
- Problem: How to test NiH_2 cells to best compare the capability of the different hydrogen electrodes?
  - *The nickel electrode is usually the life-limiting electrode when cycling NiH_2 cells*
  - *Typically, life tests are designed to stress the nickel electrode through higher depths of discharge, increased temperatures, amount or rate of overcharge, and higher currents*
- Stress factors appropriate to the H_2 electrode were proposed
  - *Increased rates for charge and discharge*
  - *Reduced temperatures to evaluate liquid and gas transport processes*
  - *Overcharge to evaluate O_2 recombination tolerance*

Hydrogen Electrode Stress Test Cycle

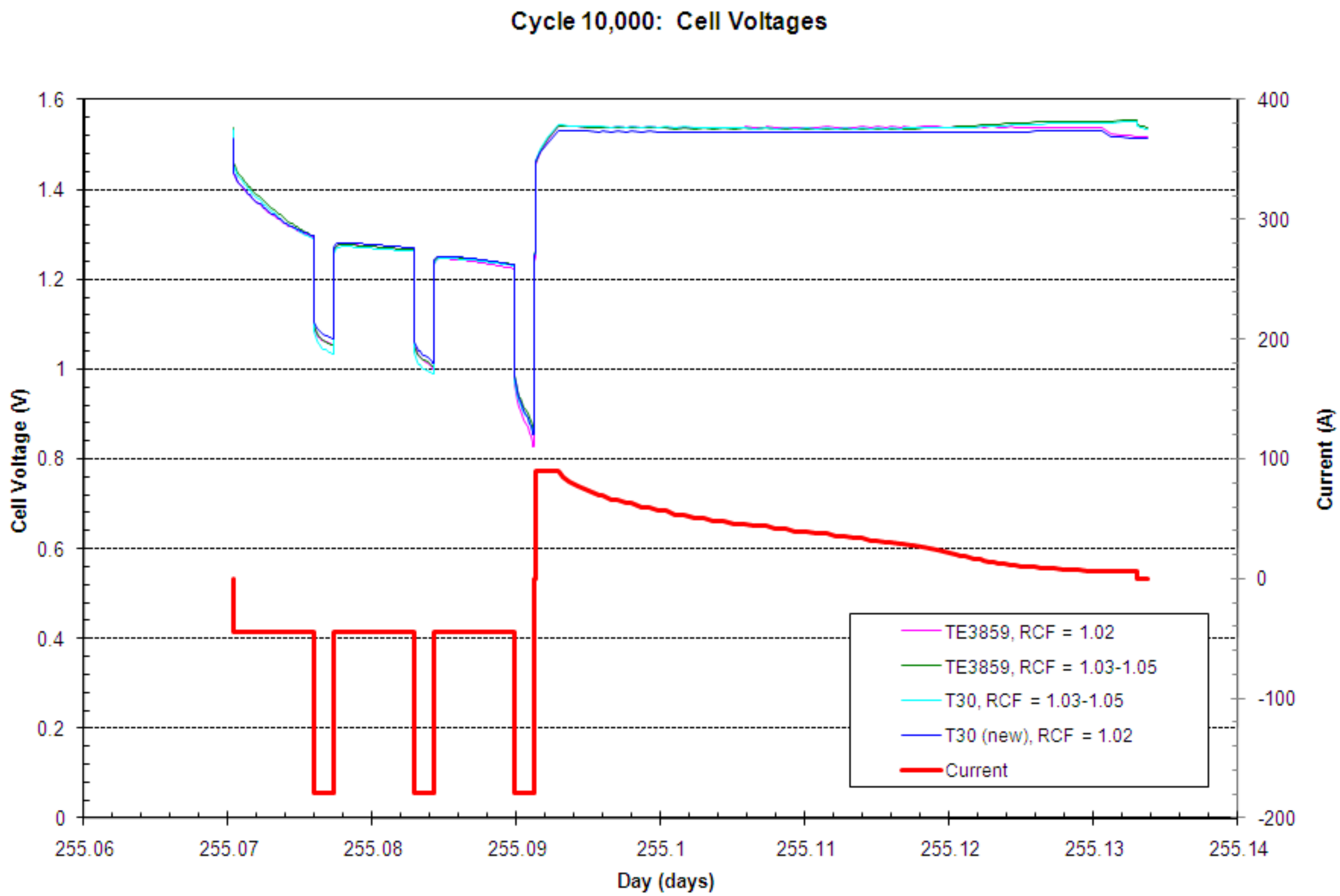
- Low temperature operation: -10ºC at end of charge
  - *Enables operation with minimal overcharge to stress the nickel electrodes*
  - *Worst case for transport processes*
  - *Relatively abrupt onset for oxygen evolution at full charge*

- 40% DOD with periodic high rate discharge pulses
  - *Three cycles of 8 min discharge at 0.5C followed by 2 min at 2C (30 min total)*
  - *High rate pulses expected to stress the H_2 electrode transport capabilities*
  - *Pulse periodicity expected to allow H_2 pressure dependence to be studied*

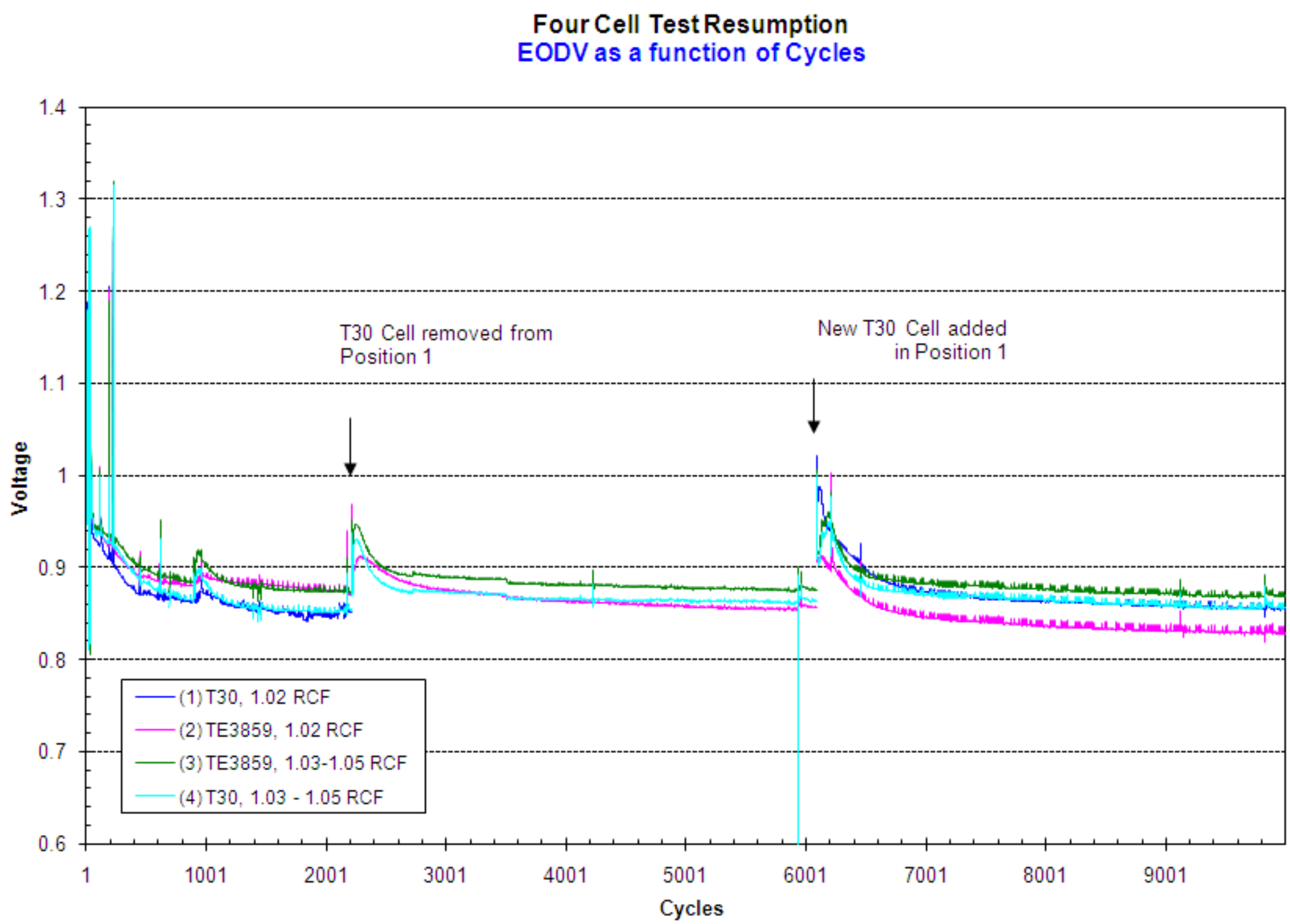
- High peak recharge rate (C-rate)
  - *Current taper at a peak cell charge voltage limit*
  - *One set of cells run at 1.02 RCF, other set at a 1.04 RCF target (1.03 – 1.05 actual)*
    - Lower RCF cells go to open circuit conditions while the second set of cells obtain their higher RCF during the 60 minute charge

- Test is planned to run until cell voltage falls below 0.7 V during 2C discharge or 1.0 V at 0.5C
  - *T30/1.02 RCF cell failure at cycle 2212 due to a set-up error*
  - *New T30/1.02 RCF cell provided at cycle 6085*
  - *To date, over 17600 cycles have been accomplished*

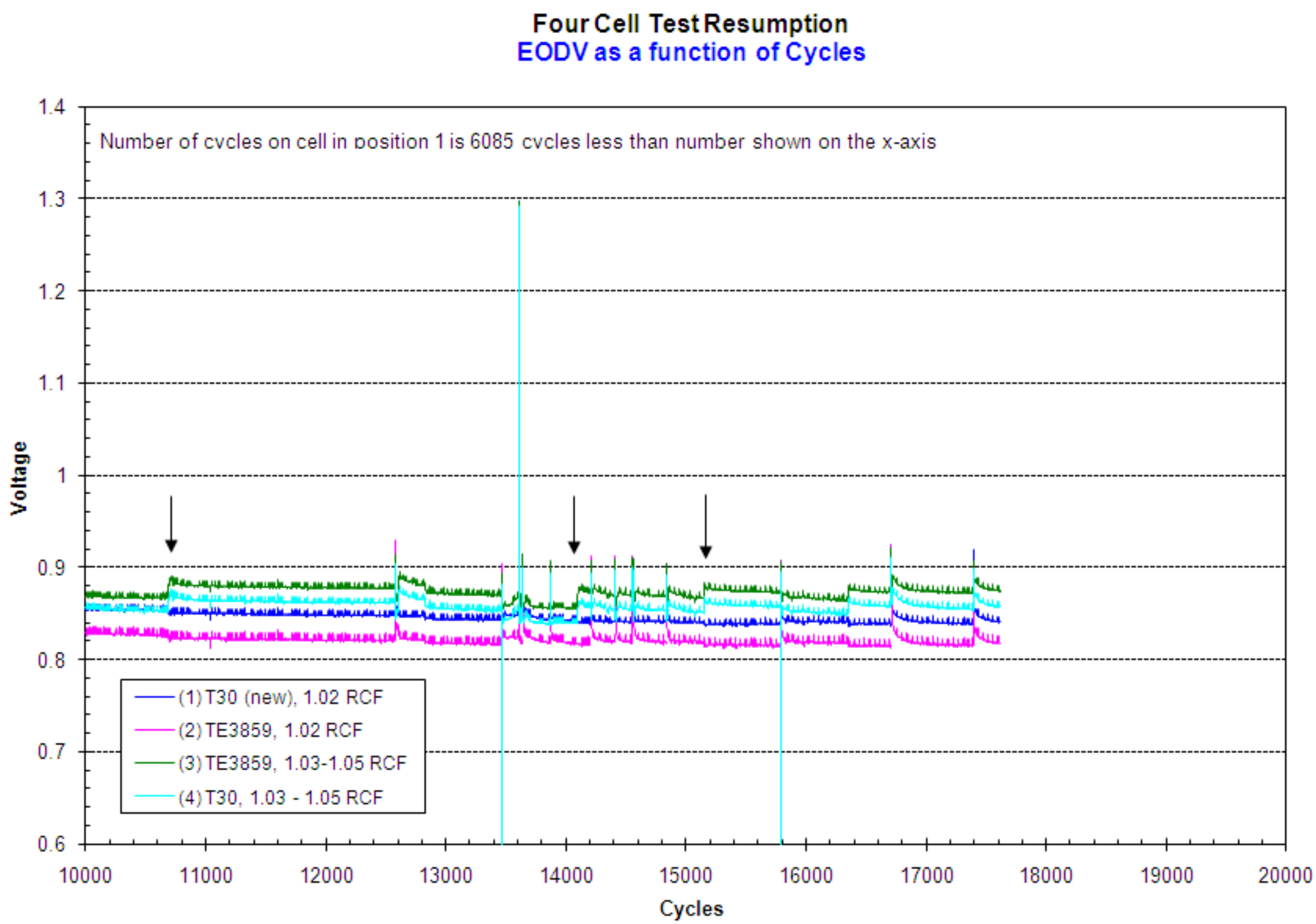
Typical Charge/Discharge Cycle: Cycle 10,000



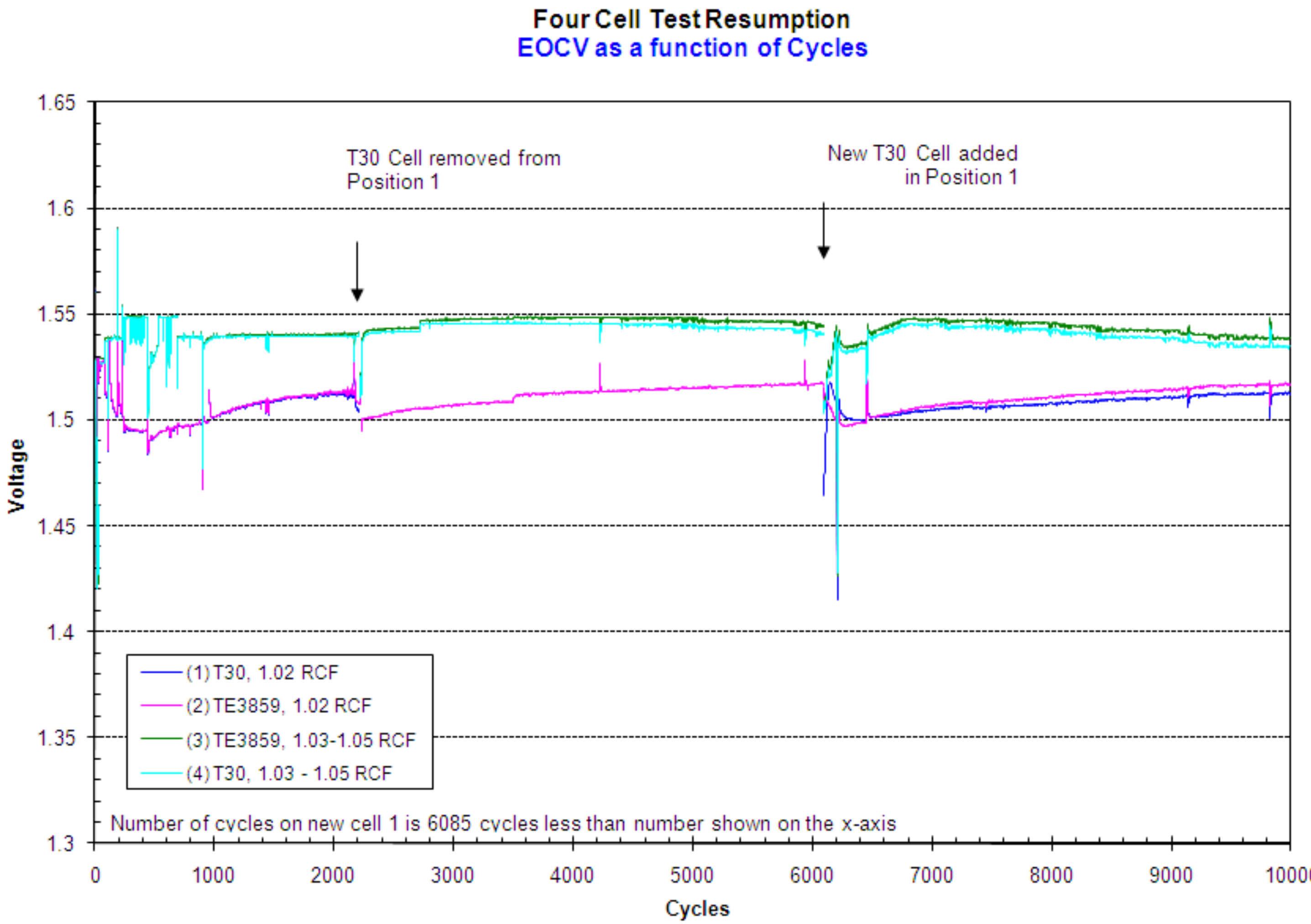
Stress Test Results to Date: EODV - first 10,000 cycles



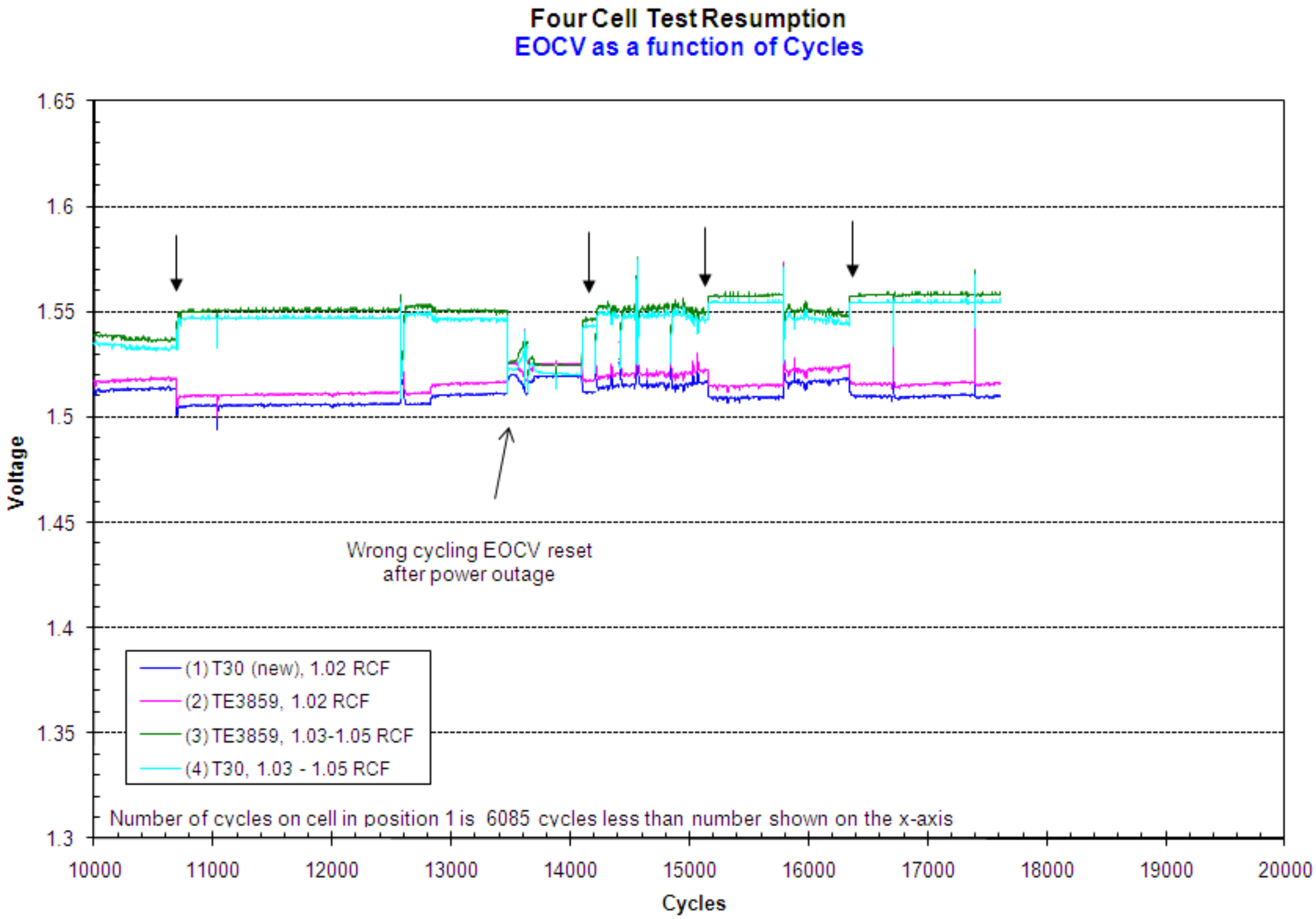
Stress Test Results to Date: EODV - 10,000 cycles to Present



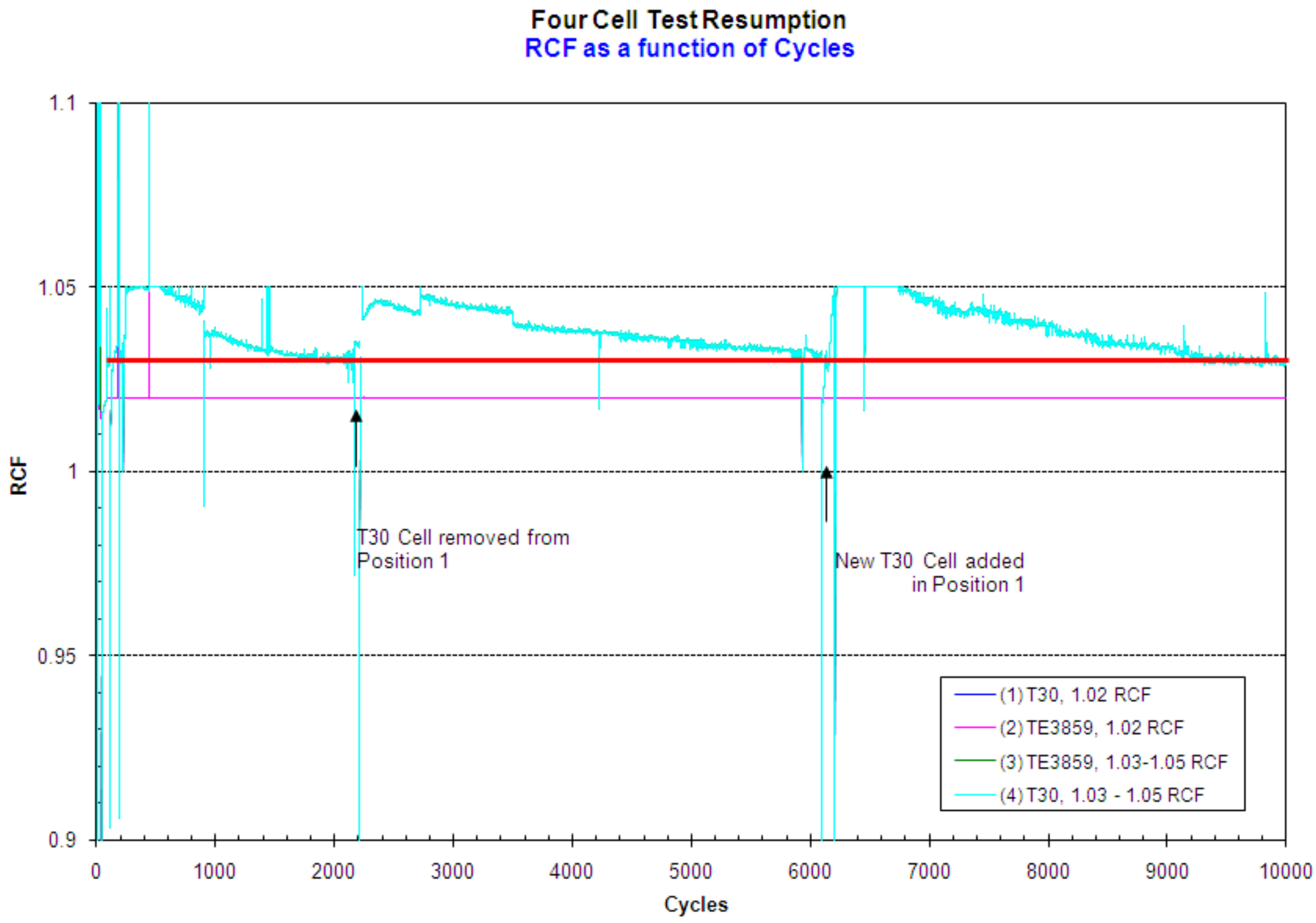
Stress Test Results to Date: EOCV - first 10,000 cycles



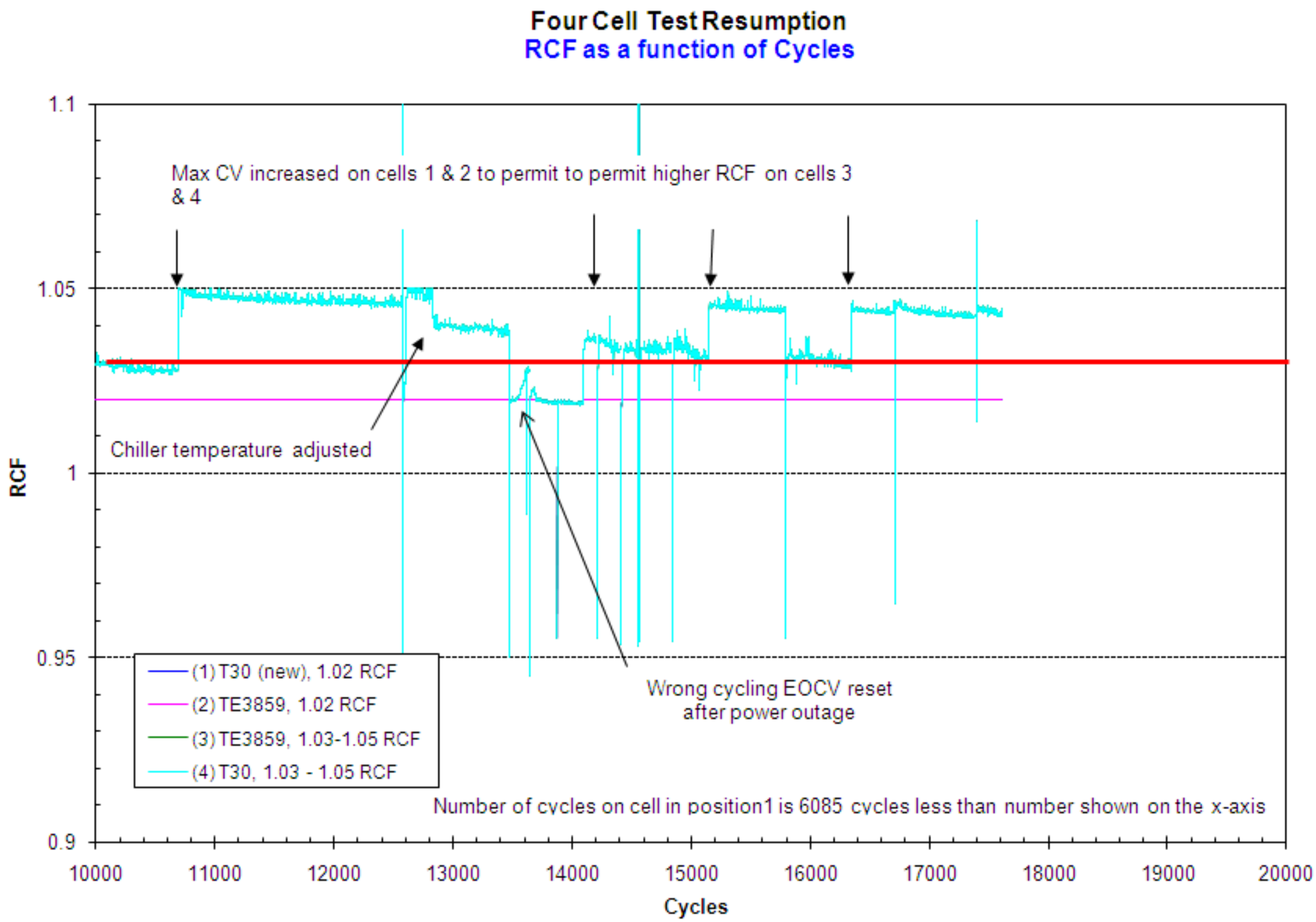
Stress Test Results to Date: EOCV - 10,000 cycles to Present



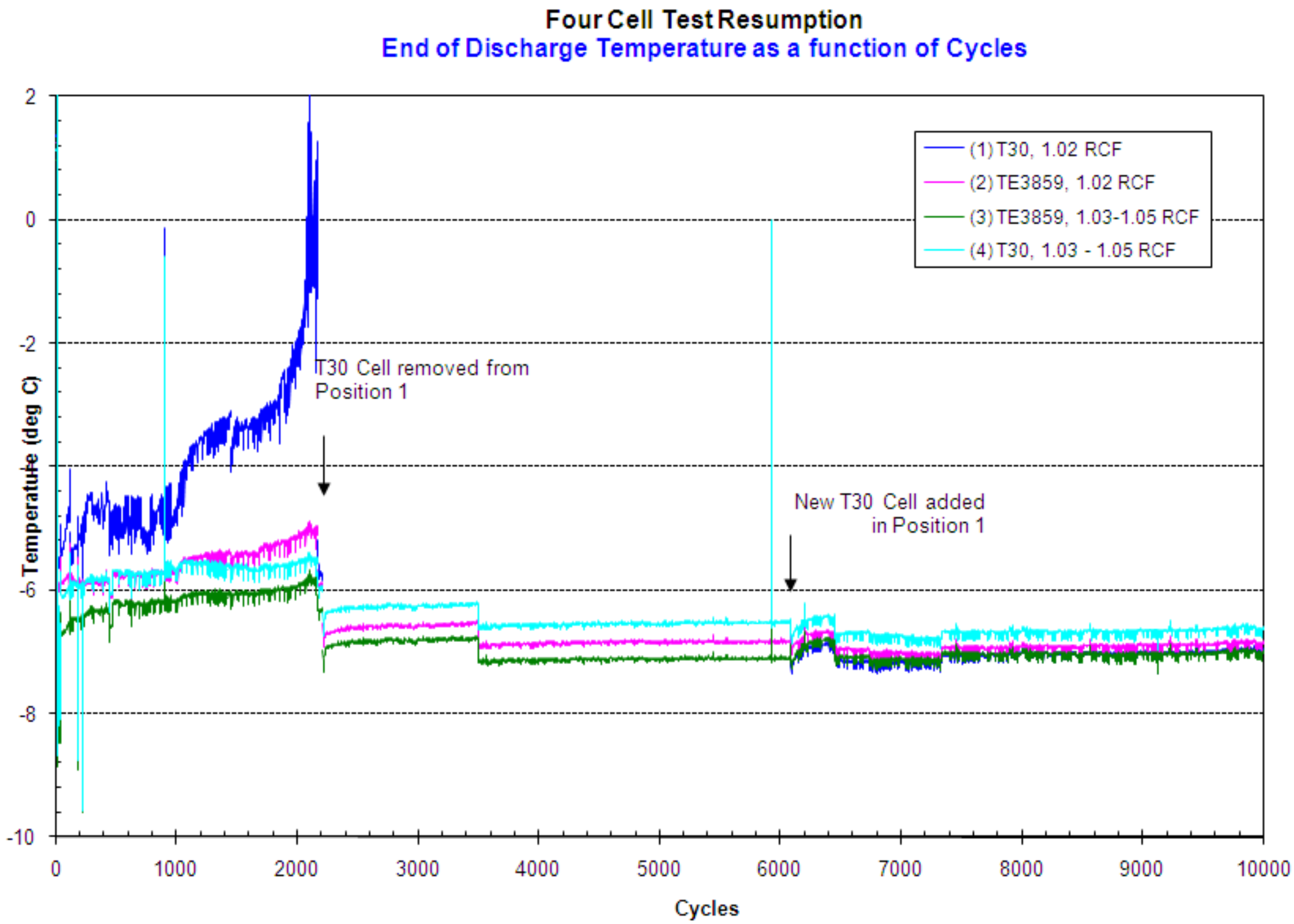
Stress Test Results to Date: RCF - first 10,000 cycles



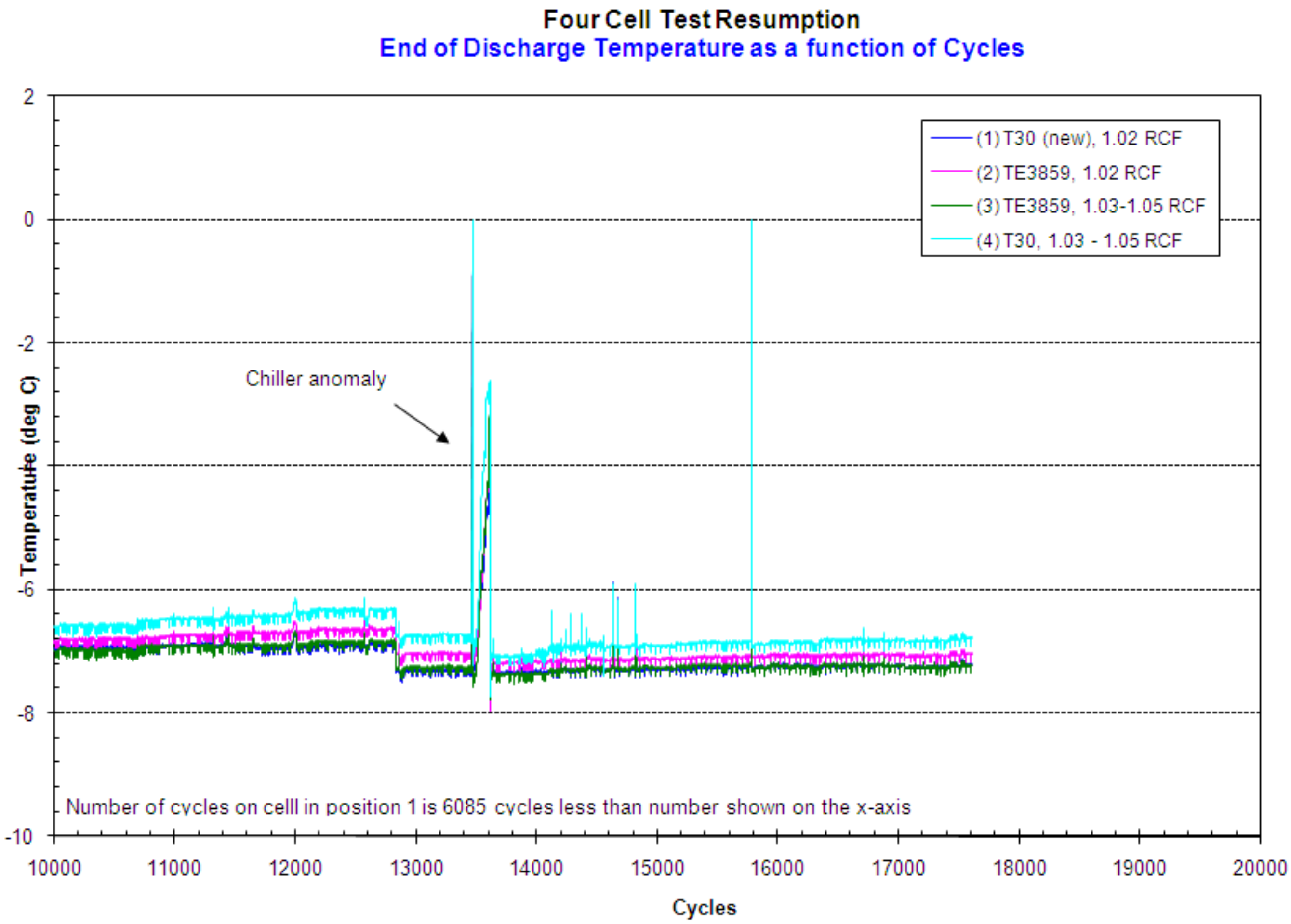
Stress Test Results to Date: RCF - 10,000 cycles to Present



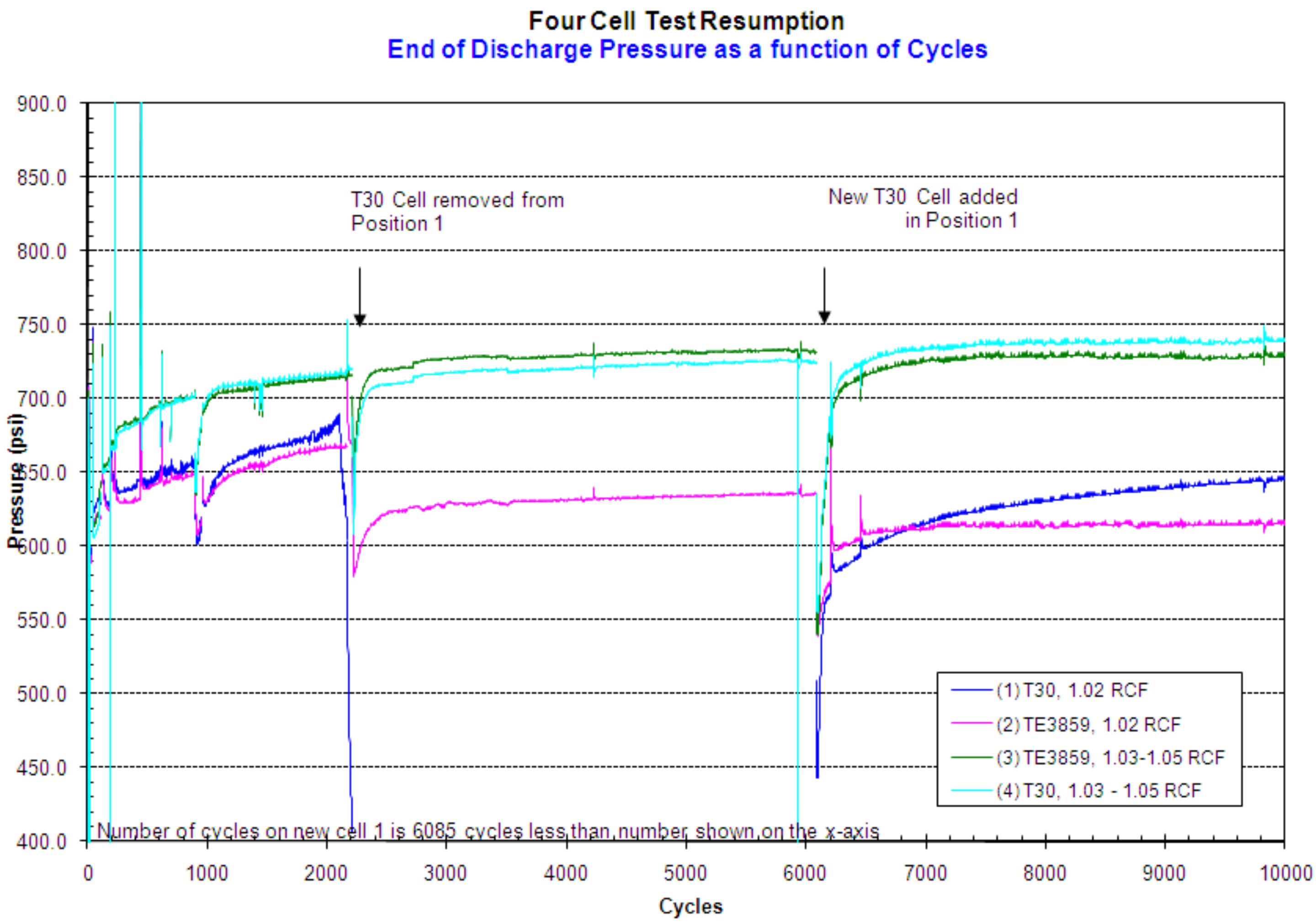
Stress Test Results to Date: EODT - first 10,000 cycles



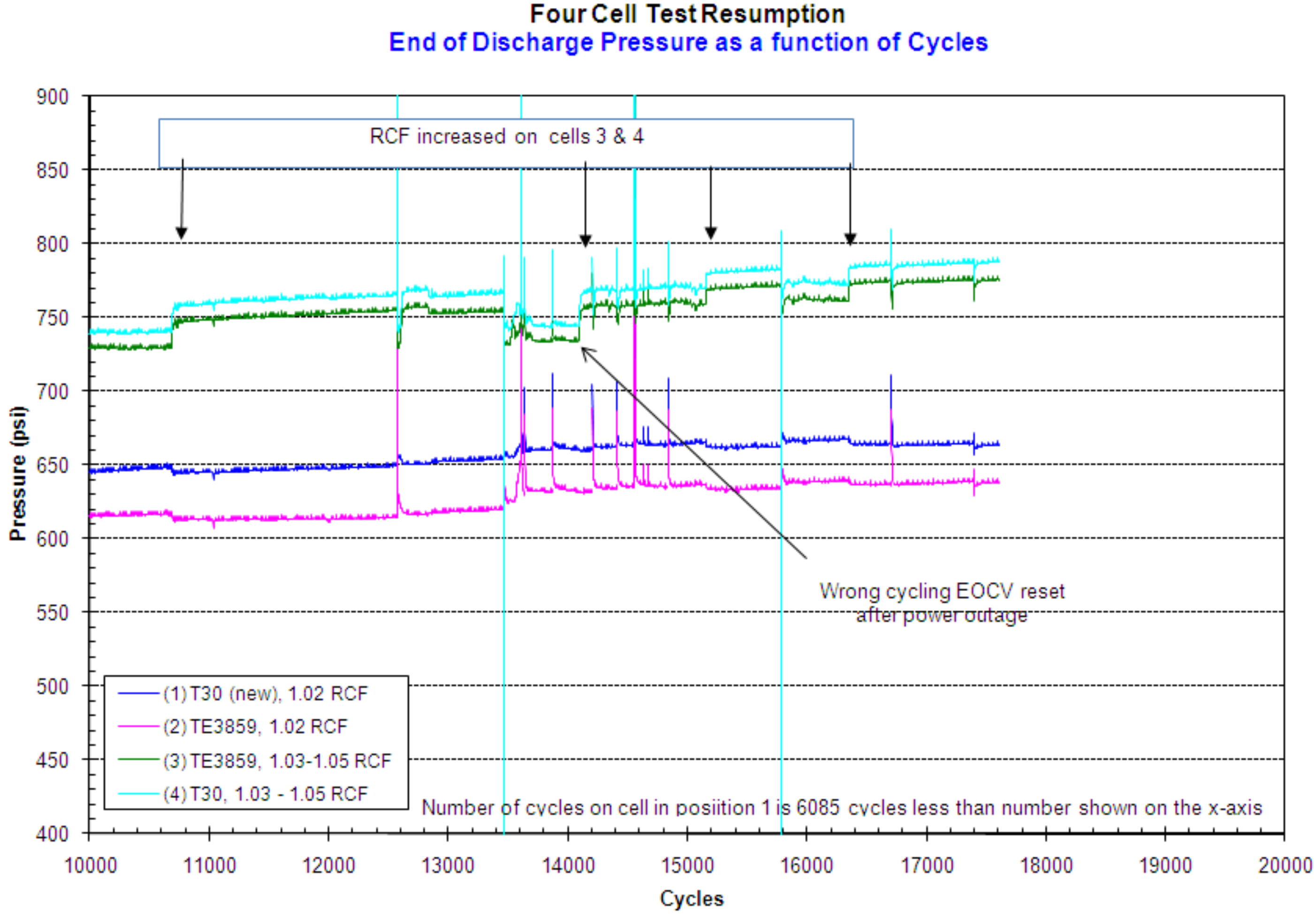
Stress Test Results to Date: EODT - 10,000 cycles to Present



Stress Test Results to Date: EODP - first 10,000 cycles



Stress Test Results to Date: EODP - 10,000 cycles to Present



Summary of Findings in the Stress Tests to Date

- Performance trends appear nominal to 17,600 cycles
  - *No unusual observations on the TE3859 cells…*
  - *…but cells still have a long way to go to approach expected cycle life limits*
- However, the goal of this test is not to demonstrate cycle life but instead encourage wear-out of the hydrogen electrode
  - *Upon failure, test and DPA will be used to determine whether it occurred on the hydrogen electrode…*
  - *…and if so, whether the type of emulsion used influenced the wear-out mechanism or rate*
- Tests may be stopped prior to reaching the 0.7V limit to characterize the hydrogen electrodes from these cells as 2013 approaches
  - *If more is known about how these electrodes age, then it may be easier and faster to run similar tests on the plate level on electrodes made from other candidate emulsions.*

Conclusions

- There is no single go-forward plan for supplying hydrogen electrodes for nickel-hydrogen cells in 2013+
- The purpose of this paper has been to review the different strategies available to extend nickel-hydrogen battery production, and the considerations found for each.
- The major focus areas being actively studied are:
  - *The aging and characteristics of T30 emulsion under different storage conditions*
  - *Chemical, material and electrical properties of candidate emulsions and electrodes made with candidate emulsions (as they come available)*
  - *The cycle tests on ISS cells activated 5+ years ahead of need*
  - *Stress tests on comparison cells of T30 and TE3859 as proof of concept*

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  - *NASA-Glenn: Penny Dalton*

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References

- Margot Wasz, Albert H. Zimmerman, “The Effect of Teflon Emulsion on Hydrogen Electrode Properties and Performance in Nickel-Hydrogen Cells,” *The 2007 NASA Aerospace Battery Workshop,* Nov. 2007.